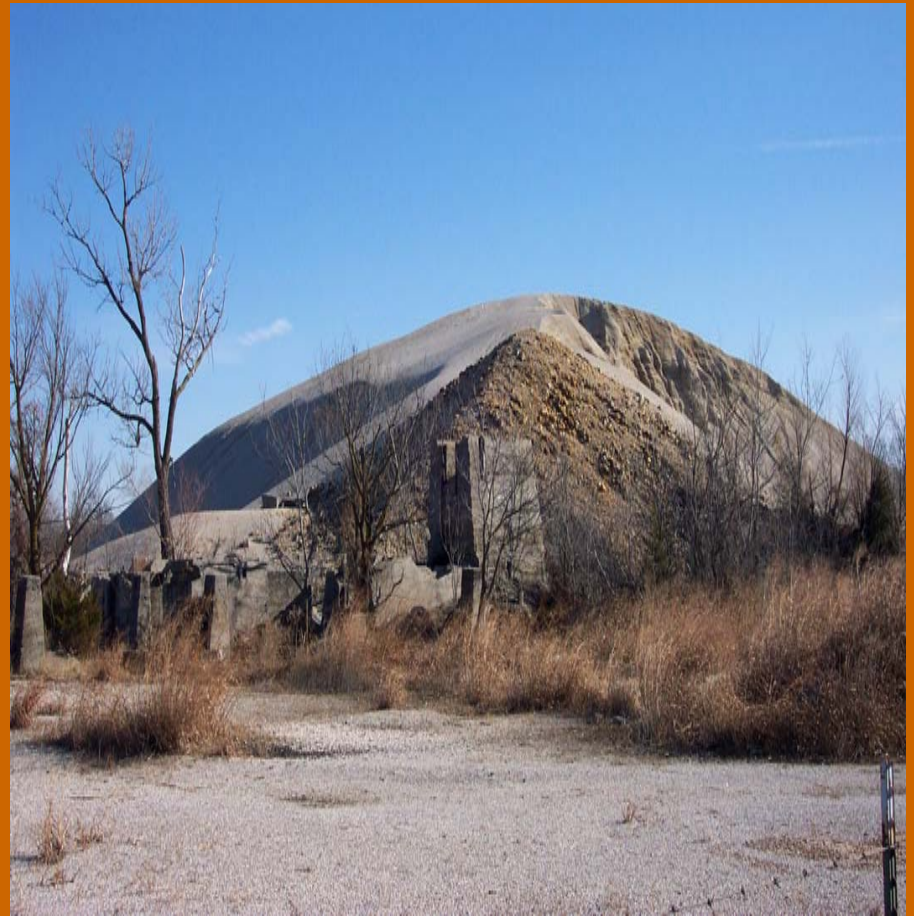


An Investigation of the Possibility of Mixing of Waters in After-Action Monitoring Wells at the Tar Creek Superfund Site –

Quapaw Tribe of Oklahoma

Introduction

- Tar Creek site is part of the Tri-State Mining District which comprises approximately 300 sq. mi. in Missouri, Kansas, and Oklahoma.
- Principal metals mined were lead and zinc.
- Mining peaked in Missouri around 1916, then shifted to Kansas and Oklahoma where it finally ceased in the 1970s.



TRI-STATE LEAD-ZINC DISTRICT

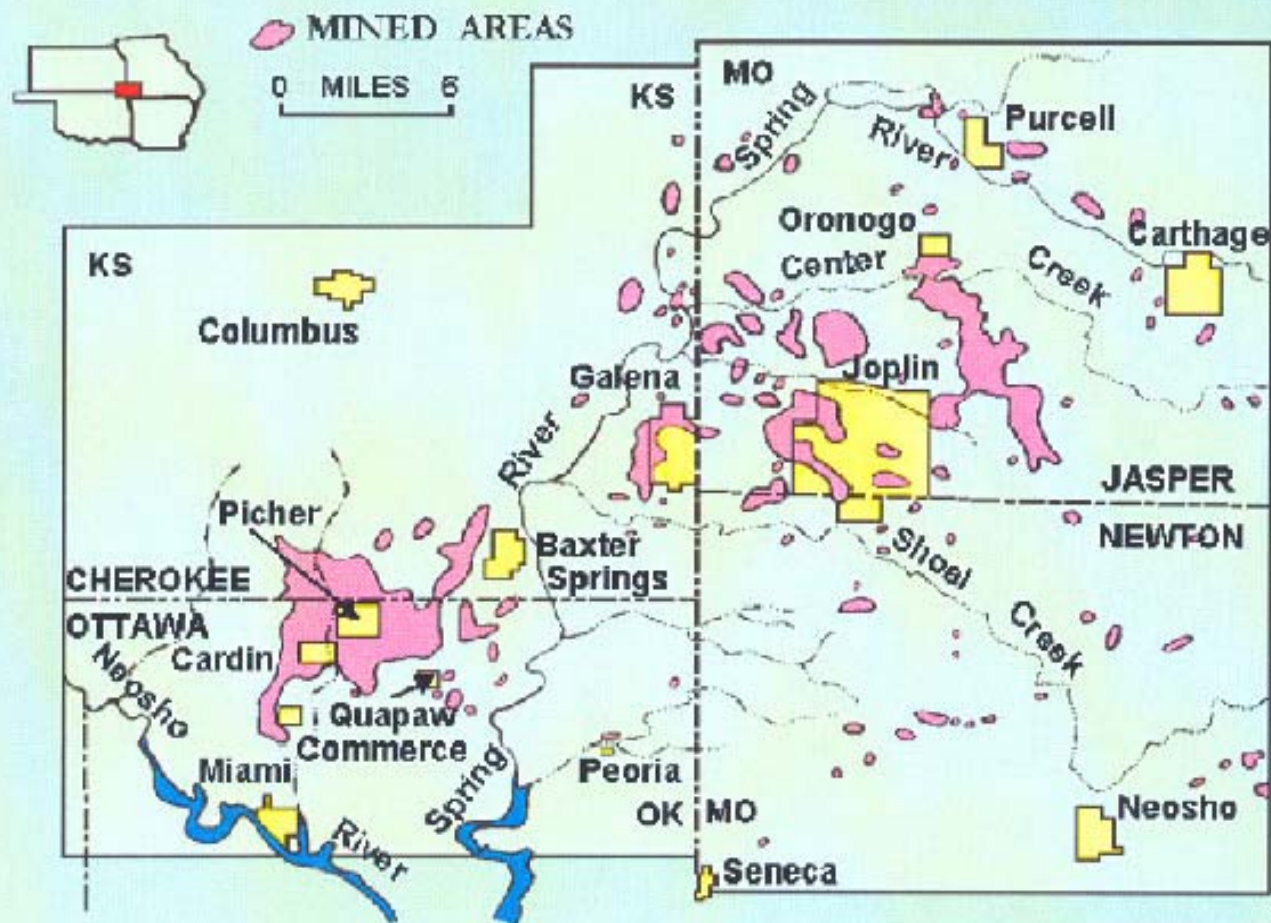


Figure 2.1

PROJECT
Picher Mining Field Subsidence Evaluation
DRAWING TITLE

Tri-State Lead Zinc District

Tribal Involvement

- **Nine tribes were moved to NE Oklahoma from various areas of the country by treaty in the 1800s.**
- **The Quapaw Tribe was moved to northeast Oklahoma from their ancestral homelands in what is now Arkansas and eastern Oklahoma through a series of treaties in the 1800s**
- **Lead and Zinc discovered on Quapaw tribal lands in the early 1900s.**

TRIBES IN OTTAWA COUNTY



Groundwater Resources

- Two major aquifers-
 - 1) Shallow: Boone Ls. (Mississippian)
Mined zone 100-300 ft.
 - 2) Deep: Roubidoux (Ordovician)
sandstone and dolomite. Overlain by shale aquitard. Municipal water supply.

Table 1. Generalized geologic nomenclature and water-yielding characteristics of Ordovician-age and younger rocks in Ottawa County
(Modified from Christensen, Pardue, and Fairchild (1994, table 1). L/s, liters per second)

System	Geologic unit	Thickness (meters)	Lithologic description	Water-yielding characteristics
Pennsylvanian	Pennsylvanian rocks, undivided	0-60	Shale, siltstone, sandstone, limestone, and a few thin coal seams.	Wells yield less than 3 L/s.
Mississippian	Mississippian rocks, undivided	0-30	Limestone, shale, siltstone, and sandstone.	Wells yield less than 1 L/s.
	Boone Formation	80-110	Chert and fine- to coarse-grained gray, light gray, and bluish limestone.	Wells generally yield less than 1 L/s but may yield as much as 50 L/s.
	Northview Shale and Compton Limestone	0-10	Greenish black or dull blue shale, and gray, nodular, shaley limestone.	Does not yield significant quantities of water to wells.
Devonian and Mississippian	Chittenango Shale	0-10	Black, carbonaceous, fissile shale.	Does not yield significant quantities of water to wells.
Ordovician	Cotter Dolomite and Swan Creek sandstone	35-170	Light buff to brown cherty dolomite with several sandy and argillaceous zones; Swan Creek sandstone identified in some wells is sandstone or sandy dolomite at base.	Wells generally yield less than 1 L/s but may yield as much as 25 L/s.
	Jefferson City Dolomite	65-130	Light buff, gray, and brown very cherty dolomite.	Water-yielding characteristics not known.
	Roubidoux Formation	20-75	Light-colored, cherty dolomite with 2 or 3 layers of sandstone, 4.5 to 6 meters thick.	Principal aquifer in Ottawa County. Wells yield 6 to over 60 L/s.
	Gascouade Dolomite and Gunter Sandstone Member	8-100	Light-colored, medium to coarsely crystalline, cherty dolomite; Gunter Sandstone Member is sandstone or sandy dolomite at base.	Not known to yield significant amounts of water from geologic units above Gunter Sandstone Member. Gunter Sandstone Member yields moderate amount of water.



**Ore Deposits in the Tar
Creek Area Were Found
in the Boone Formation
(Limestone) at Depths
of 100 to 300 Ft.**



Groundwater Resources

- Groundwater pumped from mines until 1970 when mining ceased.
- As groundwater filled the mines, it became contaminated by exposed lead and zinc sulfide minerals and other sources of heavy metals.
- Due to the mines filling with water, and over-pumping of Roubidoux groundwater, there is now a downward (vertical) flow gradient from the Boone aquifer to the Roubidoux aquifer.
- This vertical gradient enhances the potential of contamination of the Roubidoux aquifer.

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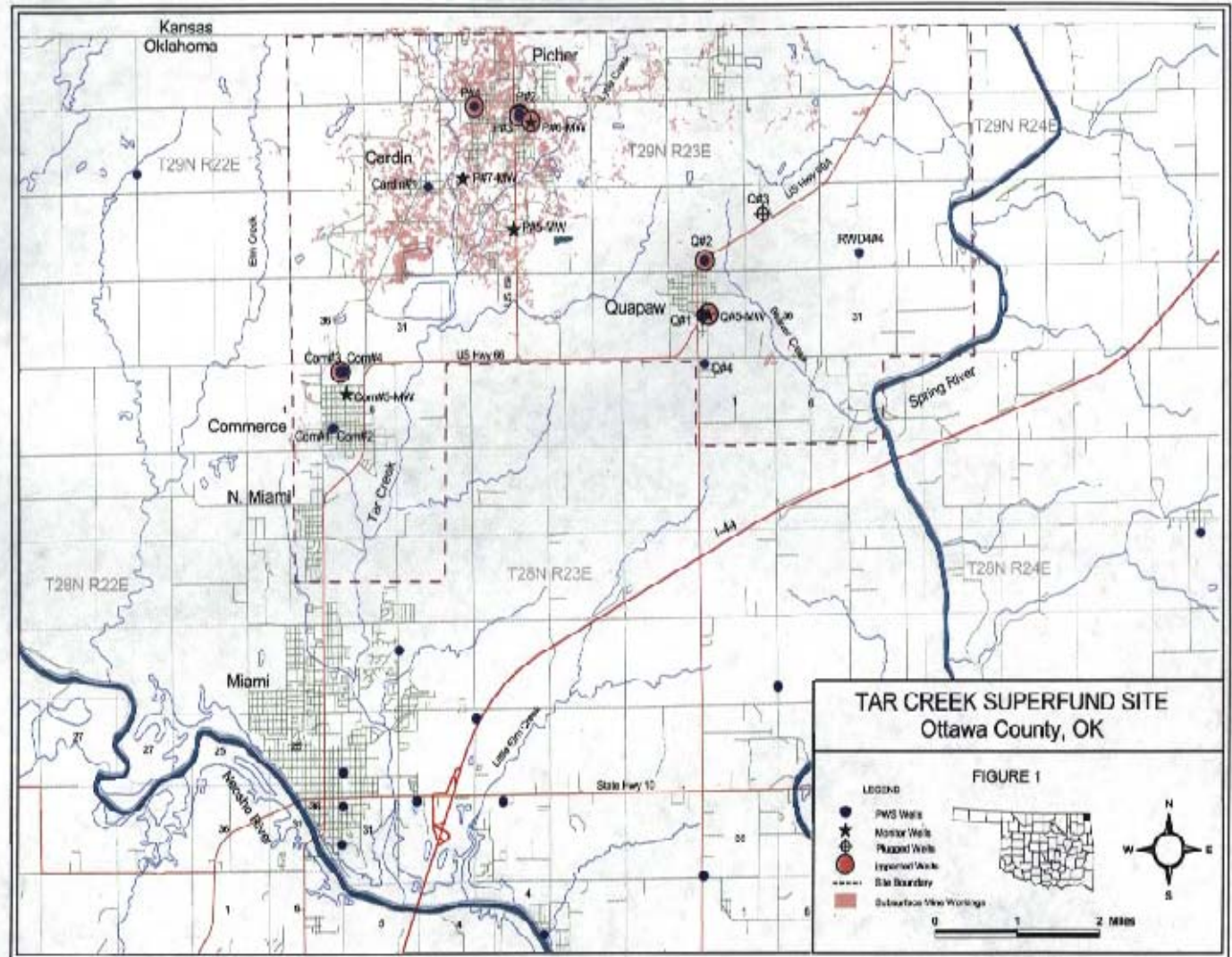
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Tar Creek Superfund Site

- Tar Creek was added to the National Priority List (NPL) of Superfund Sites in 1982.
- Site divided into several Operable Units (OUs). OU1 is surface water and groundwater.
- OU1 was addressed with surface water diversion structure and well plugging in 1980s.

Tar Creek Superfund Site

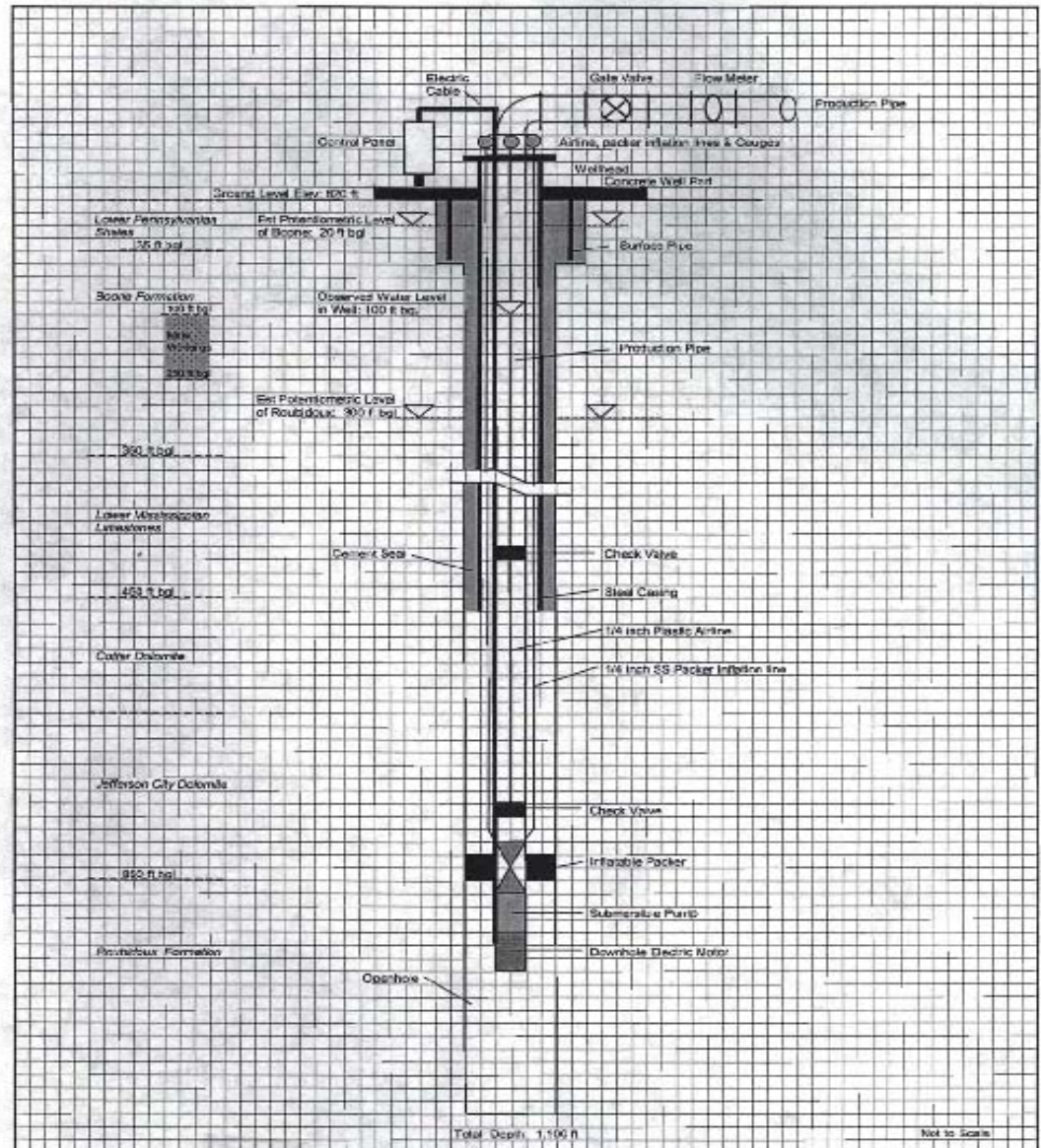
- After Action Monitoring performed by State of Oklahoma (ODEQ) began in 1992 in the form of monitoring municipal wells in the towns of Picher, Commerce, and Quapaw in 1992.
- These wells began showing elevated levels of iron, zinc, and sulfate, indicating they were being impacted by mine water.



Tar Creek Superfund Site

In 1997, ODEQ drills and completes 5 monitoring wells in the Roubidoux aquifer with state-of-the-art casing design to ensure no leakage through well annulus.

Concern about potential for mine water entering Roubidoux aquifer through poor well construction and/or natural fractures.

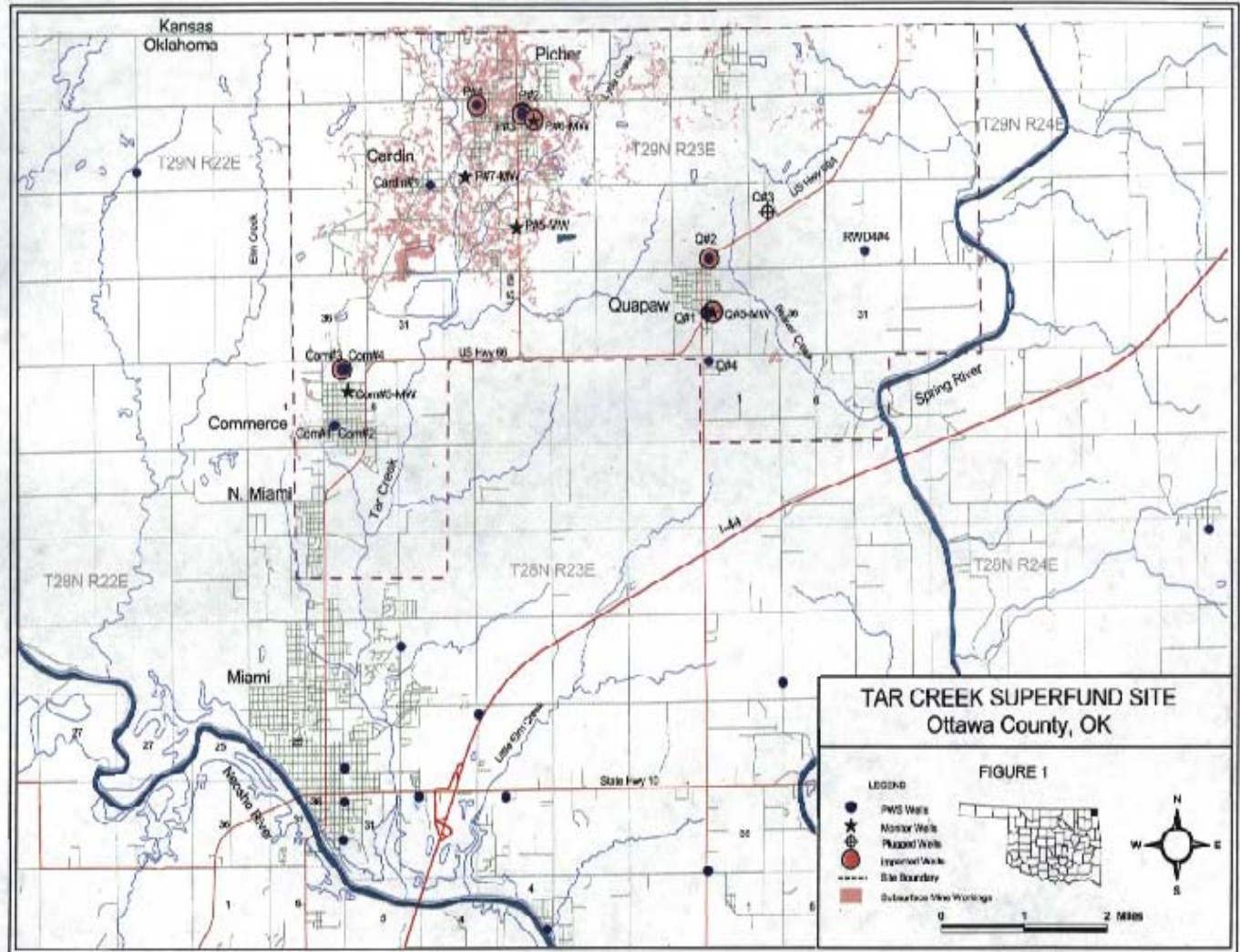


Tar Creek Superfund Site

Results of monitoring of newest wells indicate that at least two of the five show evidence of being impacted by mine water (Picher #6MW and Quapaw #5MW).

Evidence includes elevated levels of iron and sulfates.

To investigate this further, additional analysis is required.



Primary Questions

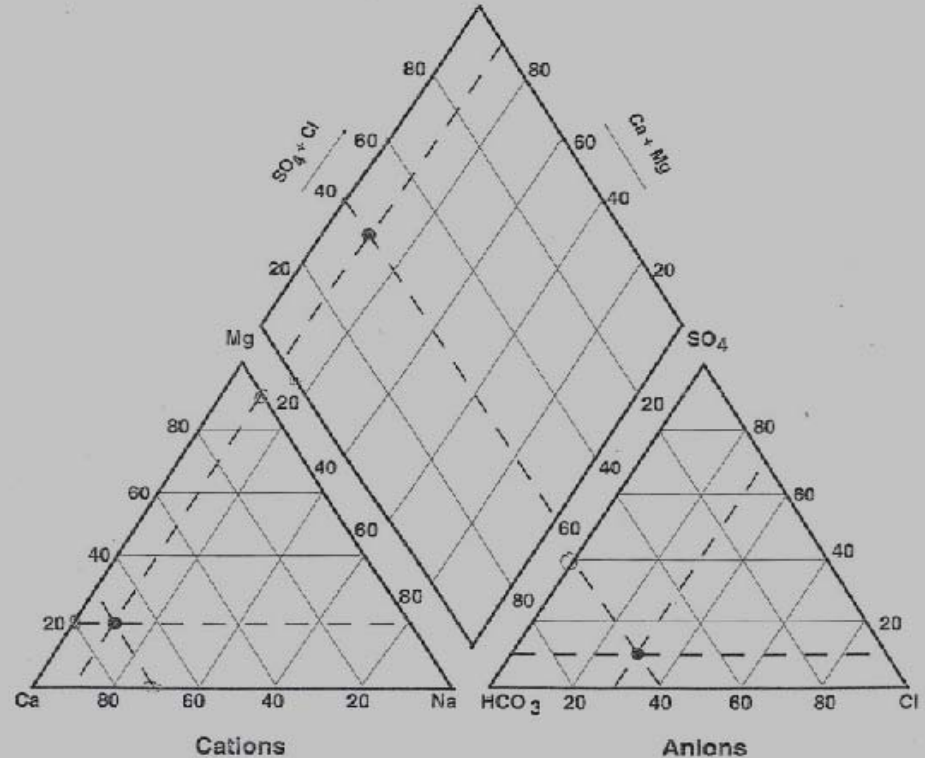
- Are monitored Roubidoux wells being impacted by mine water?
- If so, is the mine water from the Boone formation reaching the Roubidoux zone due to poor casing seals, or from natural geologic conduits (i.e. fractures)?

Evidence of Mixing

- **Technique needed to investigate possibility of mixing of mine water with clean Roubidoux aquifer.**
- **Necessary to compare chemistry of ground water sample suspected to be impacted by mine water with chemistry of non-impacted (clean) Roubidoux water and with mine water sample.**
- **Clean water from Roubidoux aquifer represented by the water from Commerce #5MW; mine water represented by USGS samples from abandoned mine shaft near Picher.**
- **Groundwater suspected of being mixed with mine water represented by water from the Picher #6MW well (remembering that this well is a new monitoring well with state-of-the-art casing design)**

Piper Diagrams

- Piper diagrams used in geochemistry and are a combination of cation and anion triangles that lie on a common baseline.
- Groundwater from common source (aquifer) has unique balance of cations and anions. One sample plots as three points on Piper Diagram.
- In this sample: cations consist of 70% Ca; 20% Mg; and 10% Na.

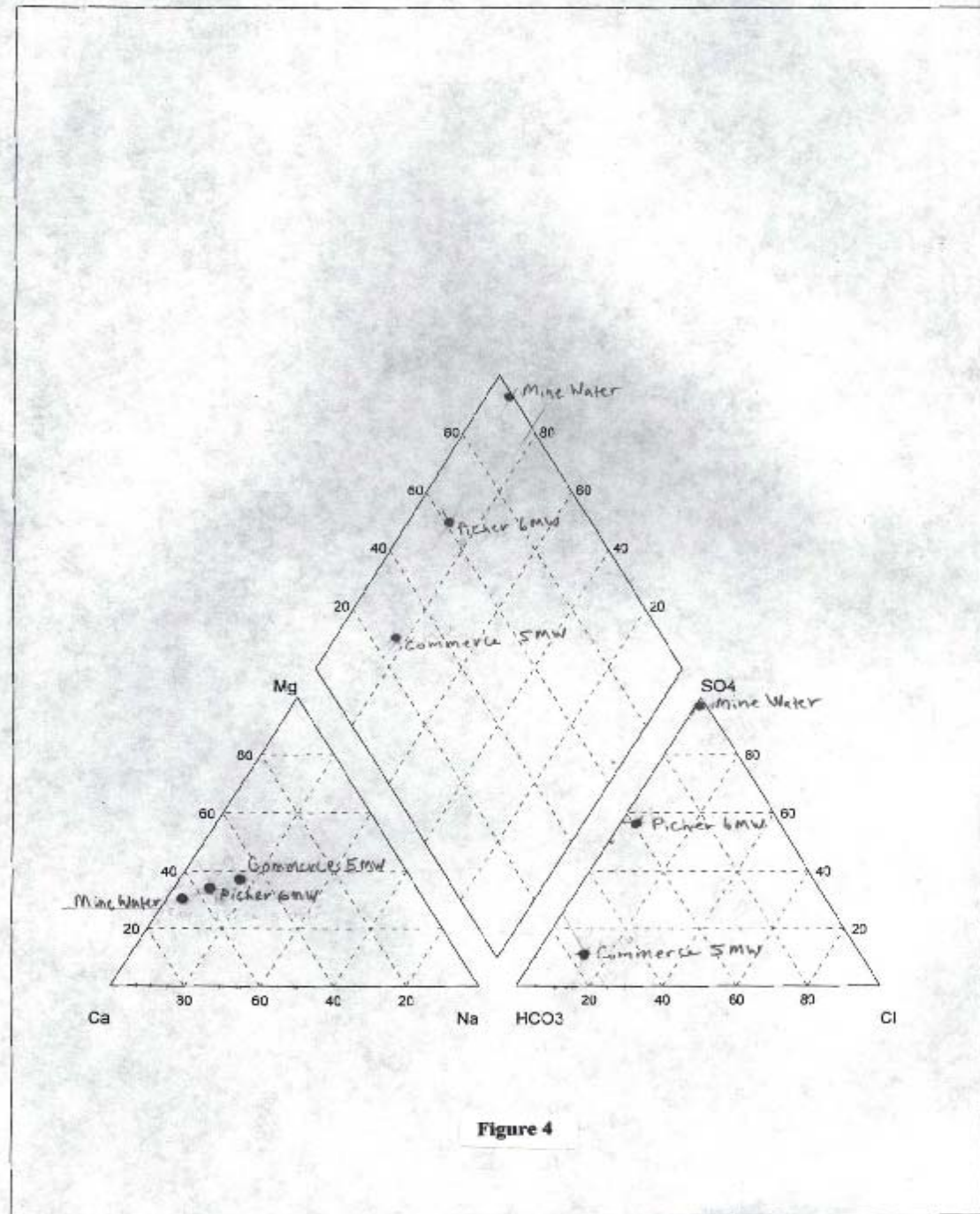


Piper Diagrams

- Piper diagrams indicate evidence of mixing if *all* of the following occur:
 - 1) the analyses plot in a straight line in the cation and anion triangles;
 - 2) the “mixture” plots between the two end members; and
 - 3) the mixture exhibits the same proportions between end members in all regions of the Piper diagram (the “mixture” plots at the same position relative to the end members in all regions of the diagram) .

Piper Diagrams

- Water quality data from the mine shaft, the Picher #6MW well, and the Commerce #5MW were plotted on a Piper diagram.
- The criteria for indicating a mixture are met. (water from the Picher #6MW well is a mixture of mine water and clean Roubidoux groundwater).



WATEVAL Computer Modeling Program

- Computer program developed by Geochemist Arthur Hunslow that has capability of analyzing and quantifying the evidence for mixing among input water analyses.
- Program utilizes the water analysis data of the end members and calculates a *predicted* mixture.
- The predicted mixture is then compared statistically to the actual mixture
- A correlation coefficient (R) is calculated to measure the level of agreement between actual and predicted mixture. A correlation coefficient of 0.9 (on a scale from 0 to 1) or higher, indicates strong evidence for mixing.

WATEVAL Computer Modeling Program

FR (conc) = 0.15337 FR (dilute) = 0.84663 R = 0.915
R2 = 0.837

	SOURCE 1 Mine	SOURCE 2 5MW	MIXTURE 6MW	CALC
Na-	1.91	0.48	0.65	0.70
K -	0.10	0.05	0.08	0.06
Ca++	23.95	1.40	4.89	4.86
Mg++	11.02	1.15	3.13	2.67
Cl-	0.18	0.39	0.20	0.36
SO4--	43.10	0.36	4.98	6.91
HCO3-	0.46	2.28	3.62	2.00
TDS	80.72	6.11	17.55	

Number used in average is 7

- Water quality data from a mine shaft, the Picher #6MW well, and the Commerce #5MW were entered into WATEVAL (aquifer input data also required).

- Results indicate that water from Picher #6MW well is a mixture of mine water and clean Roubidoux groundwater (R=0.92).

Conclusions

- Refilling of Mines and over pumping of Roubidoux wells has created a downward (vertical) gradient of hydraulic head between upper aquifer (Boone formation) and lower aquifer (Roubidoux) thereby increasing the potential for mine water contaminant migration into municipal water supply.
- Use of Piper diagrams and computer modeling indicates strong evidence that mine water is impacting Roubidoux groundwater in newly drilled monitoring wells.
- The fact that mine water is impacting newly drilled monitoring wells with state-of-the-art casing design, indicates that contaminant migration is occurring through natural geologic pathways (i.e. fractures and leaky aquitard formations) rather than through conduits created by poor casing seals.

Next Steps

- ODEQ will continue to monitor wells as part of the After Action Monitoring of OU1.
- Data will be evaluated at next five-year review to determine if action is needed (i.e. if primary drinking water standards are being consistently exceeded).
- Federal buyout has been initiated of properties in danger of subsidence according to recent USCOE study. Consequently, municipal water supply wells may be abandoned.